Critical Behavior of the Second Harmonic in a Density Wave System

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We report a high resolution synchrotron x-ray study of the first- and second-harmonic order parameter and critical fluctuation scattering at a nematic–smectic-A_2 transition. The order parameter, smectic susceptibility, and correlation lengths for the fundamental, as well as the order parameter and smectic susceptibility for the second harmonic, yield critical exponents in good agreement with 3D-XY multicritical scaling theory. However, the second-harmonic correlation lengths disagree markedly with predictions of current theory for density wave systems.

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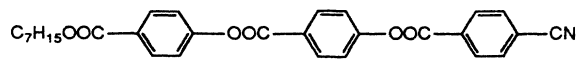
A wide variety of physical systems exhibit phase transitions involving the establishment of a density wave which may be characterized simply by its magnitude and by its phase. Examples in solids include incommensurate charge density wave (CDW) systems such as $NbSe_3$ [1] and spin density wave systems such as Cr [2]. Two-dimensional (2D) freezing from a hexatic fluid to a 2D solid is another example [3]. Complex fluids exhibiting lamellar ordering also may fall into this general class. The simplest of these is the smectic-A (Sm-A) phase of thermotropic liquid crystals [4]. The nematic (N) phase of rodlike liquid crystal molecules is orientationally ordered, but positionally disordered. The N-Sm-A phase transition corresponds to the establishment of a one-dimensional mass density wave in a three-dimensional fluid with the density wave along the direction of orientational order [4]. This broken symmetry defines the Sm-A phase. The phase transitions and critical fluctuations in such systems can be described by an order parameter $\psi e^{i\phi}$ which is associated with a sinusoidal density wave $\rho = \rho_0 + \psi e^{i\phi} e^{iq_0 z}$. Hence the critical behavior associated with fluctuations of the order parameter is expected to be XY-like. Indeed, critical x-ray scattering at the Peierls transition in the CDW system blue bronze ($K_{0.3}MoO_3$) revealed such three-dimensional (3D) XY critical fluctuations [5]. Recent high resolution x-ray scattering and ac-calorimetry experiments have also shown that many features of the N-Sm-A_1 phase transition in liquid crystals are well described by the 3D XY model although the correlation lengths exhibit weakly anisotropic critical behavior [6].

In the ordered phase of sine-wave order parameter systems not just the first harmonic but in some cases many higher order harmonics, $\psi_n e^{in\phi} e^{inq_0 z}$ with $n \geq 2$, may be observed. A theory for the critical behavior of these higher harmonics has been developed in the context of hexatic liquid crystals [7,8]. This theory describes the successive harmonics of the orientational order observed experimentally in hexatic phase transitions very well [8]. However, to date no experiments have been reported on the critical fluctuations associated with the higher harmonics of sine-wave order parameter systems. This is because higher harmonic critical scattering is typically too weak to observe experimentally. Thus very simple questions have not been answered. For example, in current theories it is typically assumed either explicitly or implicitly [3,8] that the correlation lengths for the higher harmonics must equal that of the first harmonic and this has not, as yet, been tested experimentally.

In this paper we report a high resolution x-ray scattering study of the order parameter and critical fluctuations associated with the first and second harmonics at the N-Sm-A_2 transition in the polar thermotropic liquid crystal material 4′-*n*-heptyloxycarbonylphenyl-4′-(4″-cyanobenzoyloxy) benzoate (7APCBB). This material was synthesized and first characterized at the Technical University of Berlin [9]; the sample investigated was from the same synthetic batch as that used previously for C_p measurements [10]. We find that the first-harmonic order parameter and critical fluctuations are very close to those expected for a 3D XY system with a very small correlation length anisotropy. The second-harmonic peak intensity both above and below T_c exhibits the behavior predicted by Aharony and co-workers' [7,8] multicritical scaling theory for the 3D XY model. However, the second-harmonic correlation lengths above T_c differ both in magnitude and in their critical behavior from those characterizing the first harmonic. This is in disagreement with current theoretical expectations including gauge transformation theories of the N-Sm-A transition [11] and remains unexplained. These results should have consequences for the theoretical description of all 3D density wave phase transitions and possibly 2D systems as well.

The compound 7APCBB has the structure



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and the phase transition sequence is [9,10]

$$I \underset{482\,K}{\longrightarrow} N \underset{415.8\,K}{\longrightarrow} \text{Sm-}A_2 \underset{413.3\,K}{\longrightarrow} \text{Sm-}C_2.$$

The Sm-A_2 phase has a bilayer structure with the layer thickness $d=2L$, where L is the molecular length. The Sm-C_2 phase is the analogous tilted bilayer. The nematic temperature range is quite wide for this system, implying that the nematic order parameter should be well saturated close to the N-Sm-A_2 transition; hence, this transition is expected to be second order and 3D-XY-like. This has been confirmed by a high resolution calorimetric study [10]. Analysis of $C_p(N\text{-Sm-}A_2)$ data yielded the critical exponent $\alpha=-0.029$ when α was a freely adjustable parameter, and a statistically equivalent fit was obtained with α fixed at the 3D XY value ($\alpha=-0.007$).

X-ray scattering data in the nematic phase were taken on the IBM-MIT beam line X20B at the National Synchrotron Light Source at Brookhaven National Laboratory. The diffraction experiment utilized a triple-axis spectrometer with a bent Si(111) monochromator and flat Si(111) analyzer together with horizontal and vertical collimating slits. The consequent instrumental longitudinal resolution was 3.54×10^{-4} Å^{-1} half width at half maximum (HWHM), the transverse in-plane resolution was $<10^{-5}$ Å^{-1}, while the out-of-plane resolution was 0.02 Å^{-1} HWHM. The scattering intensity in the Sm-A_2 phase was relatively strong. Therefore measurements could be carried out using the Cu $K\alpha$ radiation of a Rigaku rotating-anode x-ray source on the same spectrometer. The sample was sealed in a beryllium cell having a temperature stability of better than 0.002 K, and an applied magnetic field of 0.65 T aligned the nematic director in the scattering plane, resulting in a mosaicity in the Sm-A_2 phase of 0.3° (HWHM). A linear drift of ~-0.006 K/h in the transition temperature T_c was observed and this was taken into account in the data reduction. As expected theoretically and as demonstrated in previous experiments [12], such T_c drifts have no effect on the observed critical behavior.

In the nematic phase we observed two diffuse peaks at $(0,0,q_0)$ and $(0,0,2q_0)$ with $q_0=0.1080$ Å^{-1}. The experimental procedure was that a complete set of scans was carried out at both q_0 and $2q_0$ at each temperature and the temperature was then increased to the next value. Several such sweeps were done during the experiment. The value of T_c was determined frequently during the experiment by observing the onset of smectic mosaicity for the q_0 peak. Figure 1 shows typical longitudinal ($q_\parallel$) and transverse ($q_\perp$) scans through the q_0 and $2q_0$ peaks at ~10 mK above T_c. The marked difference in magnitude between the integrated intensities of the q_0 and $2q_0$ peaks shown in Fig. 1 suggests strongly that the transition is driven by layer formation of antiparallel dimer pairs of dipolar molecules. It is immediately evident from Fig. 1 that the scans at $2q_0$ are much broader than those at q_0, which implies that the relevant correlation lengths of the

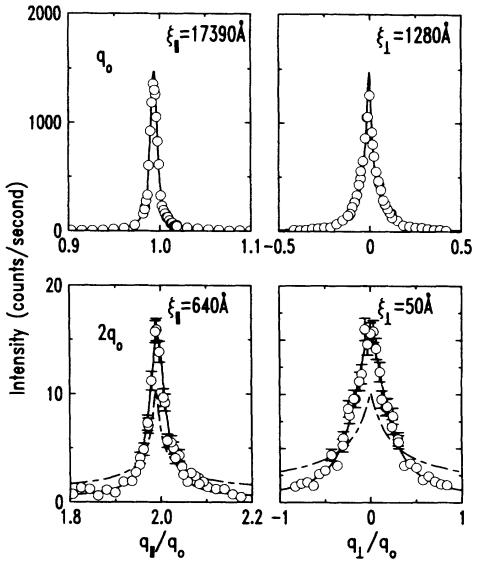

FIG. 1. Longitudinal and transverse x-ray scans through the q_0 and $2q_0$ peaks in 7APCBB at $T-T_c=0.010$ K for q_0 and 0.013 K for $2q_0$. The solid lines are the results of least-squares fits by Eq. (1) convoluted with the instrumental resolution function. The dashed lines for the $2q_0$ scans correspond to the results of least-squares fits by Eq. (4) with $\eta_2=1.4$.

$2q_0$ fluctuations are much shorter than those of the q_0 fluctuations. Thus, even without any analysis, it is clear that the theoretical assumption that the correlation lengths for the successive harmonics are identical cannot be correct. We now discuss quantitative analysis of the measurements.

Above T_c, fluctuations in the components of the order parameter $\psi_n e^{in\phi}$ give rise to critical scattering which can be described by the x-ray structure factor [13]

$$S(\mathbf{q})=\frac{k_B T\chi_n}{1+\xi_{\parallel n}^2(q_\parallel-nq_0)^2+\xi_{\perp n}^2 q_\perp^2+c_n\xi_{\perp n}^4 q_\perp^4} \qquad (1)$$

convoluted with the instrumental resolution function. χ_n is the susceptibility and $\xi_{\parallel n}$ and $\xi_{\perp n}$ are the correlation lengths along the longitudinal and transverse directions associated with a given order parameter $\psi_n e^{in\phi}$. The quartic term, needed to describe the non-Lorentzian transverse line shape for the q_0 fluctuations, has a freely adjustable coefficient c_n. We find that c_1 exhibits the same kind of temperature dependence seen typically for N-Sm-A_1 and other N-Sm-A [14] systems while the $2q_0$ profiles are well described by pure Lorentzians; that is, $c_2=0$ within the errors. Simultaneous fits of the longitudinal and transverse scans yielded $(\chi_1,\xi_{\parallel1},\xi_{\perp1})$ and $(\chi_2,\xi_{\parallel2},\xi_{\perp2})$ for the peaks around q_0 and $2q_0$, respectively.

Susceptibility and correlation lengths for the q_0 peak and the $2q_0$ peak in the nematic phase are shown in Figs. 2(a) and 2(b) together with power law fits using $\chi(t)=\chi_0 t^{-\gamma}$, $\xi_\parallel(t)=\xi_\parallel^0 t^{-\nu_\parallel}$, and $\xi_\perp(t)=\xi_\perp^0 t^{-\nu_\perp}$, where

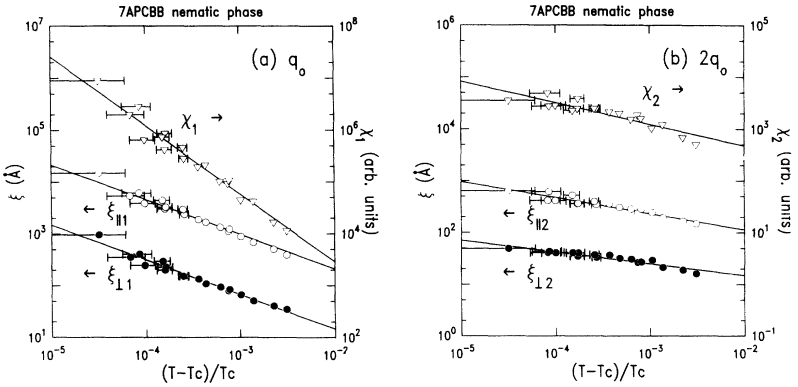

FIG. 2. (a) Sm-A_2 susceptibility χ_1 and the longitudinal and transverse correlation lengths $\xi_{\parallel 1}$ and $\xi_{\perp 1}$ for the first harmonic at q_0 in the nematic phase of 7APCBB. The solid lines are single power laws with 3D XY exponents $\gamma_1=1.316$, $\nu_{\parallel 1}=\nu_{\perp 1}=0.669$; (b) same quantities for the second harmonic at $2q_0$. The lines represent the results of power law fits (see text) with $\gamma_2=0.41$, $\nu_{\parallel 2}=0.31$, and $\nu_{\perp 2}=0.23$. All errors in χ and ξ are less than the size of the plotted symbols. Data from several runs are superimposed.

$t=(T-T_c)/T_c$. For all of the data, the 1 standard deviation errors in χ and ξ are smaller than the size of the plotted symbols. However, $T-T_c$ has a typical uncertainty of 0.012 K due to the combined effects of the uncertainties in T_c in a given run and the T_c drift rate. For the q_0 peak, the least-squares values of the critical exponents and amplitudes are $\gamma_1=1.34\pm0.14$, $\nu_{\parallel 1}=0.70\pm0.07$ and $\xi^0_{\parallel 1}=7.0$ Å, $\nu_{\perp 1}=0.64\pm0.07$, and $\xi^0_{\perp 1}=0.83$ Å. These exponent values agree within the errors with the 3D XY values $\gamma_{XY}=1.316\pm0.002$ and $\nu_{XY}=0.669\pm0.001$ [15], and the length anisotropy itself is quite small, $(\nu_\parallel-\nu_\perp)_1=0.06\pm0.03$. The latter is obtained from fits to $\xi_{\parallel 1}/\xi_{\perp 1}$ directly. In order to stress how close these q_0 results are to 3D XY behavior, the lines shown in Fig. 2(a) represent fits with exponent values fixed at XY values $\gamma=\gamma_{XY}$, $\nu_{\parallel 1}=\nu_{\perp 1}=\nu_{XY}$. Power law fits to the χ_2, $\xi_{\parallel 2}$, and $\xi_{\perp 2}$ values obtained from the $2q_0$ diffuse peak yield much different exponents: $\gamma_2=0.41\pm0.09$, $\nu_{\parallel 2}=0.31\pm0.04$, and $\xi^0_{\parallel 2}=27.1$ Å, $\nu_{\perp 2}=0.23\pm0.04$ and $\xi^0_{\perp 2}=5.2$ Å, and $(\nu_\parallel-\nu_\perp)_2=0.08\pm0.04$. The error bars represent 1 standard deviation statistical errors together with the effects of the uncertainty in T_c. From the relative temperature dependences it is readily deduced that the scattering at $2q_0$ arises from intrinsic second-harmonic fluctuations rather than independent Sm-A_1 fluctuations or multiple scattering. The ratio of scattering wave vectors $2q_0/q_0$ is 2.000 ± 0.003 both above and below T_c with no systematic temperature dependence. The ratio of diffuse intensities χ_2/χ_1 varies from $\sim4\times10^{-2}$ at $t=3\times10^{-3}$ (where the q_0 fundamental scattering is quite weak) to $\sim4\times10^{-4}$ at $t=3\times10^{-5}$.

In addition to studying the diffuse scattering above T_c, we have measured the integrated intensity $I(q_n)=\int d\mathbf{q}\,S(\mathbf{q}-n\mathbf{q}_0)$ of the quasi-Bragg peaks in the Sm-A_2 phase. The temperature dependences of $I(q_0)$ and $I(2q_0)$ are shown in Fig. 3, where the same arbitrary scale has been used for both intensities. Note that the ratio $I(2q_0)/I(q_0)(\sim|\psi_2/\psi_1|^2)$ in the Sm-A_2 phase is ~0.07 at $T=T_c-2$ K. This corresponds to a relative value of the order parameters of $|\psi_2/\psi_1|\sim0.26$, the uncertainty arising from the molecular form factor which is not well known (for a discussion, see Ref. [16]). This may be compared with the value of $|\psi_2/\psi_1|\leq0.001$ in the Sm-A phase of nonpolar 40.7 [16], which is typical of monolayer smectics.

The behavior of χ_2 in the nematic phase and $I(2q_0)$ in the Sm-A_2 phase can be quite well explained in terms of a scaling model for the behavior of harmonics of the free energy [7,8]: $F(t,h_n)\sim|t|^{2-\alpha}\Sigma_n g_n(h_n/|t|^{\phi_n})$ where ϕ_n is the crossover exponent for the nth harmonic. One immediately obtains

$$\psi_n=\partial F/\partial h_n\sim|t|^{2-\alpha-\phi_n}\sim|t|^{\beta_n}, \tag{2}$$

$$\chi_n=\partial^2 F/\partial h_n^2\sim|t|^{2-\alpha-2\phi_n}\sim|t|^{-\gamma_n}, \tag{3}$$

or $\beta_n=2-\alpha-\phi_n$ and $\gamma_n=-(2-\alpha)+2\phi_n$. The 3D XY value for ϕ_1 is 1.661, yielding $\beta_1=0.346$ and $\gamma_1=1.315$ as expected. The value of ϕ_2 is 1.16 ± 0.07 [7,8]. Thus $\beta_2=0.85\pm0.07$ and $\gamma_2=0.31\pm0.14$. This value of γ_2 is in good agreement with our experimental value $\gamma_2=0.41\pm0.09$. As is evident in Fig. 3, the intensities for both q_0

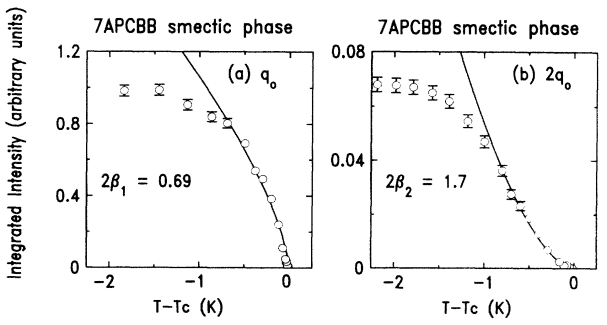

FIG. 3. (a) Bragg intensity, integrated over the central mosaicity, versus temperature at q_0. The solid line is a single power law $|T-T_c|^{2\beta_1}$ with $2\beta_1=0.69$; (b) Bragg intensity, integrated over the central mosaicity, versus temperature at $2q_0$. The Lorentz factor, $\sin2\theta$, has been removed so that the relative intensity of (b) to (a) corresponds to $\sim|\psi_2/\psi_1|^2$ times the ratio of the molecular form factors squared. The solid line is a single power law $|T-T_c|^{2\beta_2}$ with $2\beta_2=1.7$.

and $2q_0$ begin to saturate at about 1 K below T_c, presumable due to the pretransitional effects of the Sm-A_2-Sm-C_2 transition which occurred at $T_c - T = 2.5$ K in this sample. Fits of the data to single power laws for $|T - T_c| < 0.8$ K yield $\beta_1 = 0.39 \pm 0.04$ and $\beta_2 = 0.76 \pm 0.04$ in reasonable agreement with the theoretical values $\beta_1 = 0.346 \pm 0.001$ and $\beta_2 = 0.85 \pm 0.07$. To emphasize this agreement, the lines in Fig. 3 are drawn with the 3D XY values for β_1 and β_2.

The behavior of $\xi_{\parallel 2}$ and $\xi_{\perp 2}$ and the critical exponents $\nu_{\parallel 2} \simeq 0.31$, $\nu_{\perp 2} \simeq 0.23$ is more difficult to explain. The heat capacity seems to be well characterized by a single critical exponent $\alpha \simeq \alpha_{XY} = -0.007$. Thus, according to theoretical expectations, contributions to $F(t, h_n)$ due to fluctuations at q_0 and at $2q_0$ should both vary like $|t|^{2-\alpha}$. Conventional hyperscaling ideas lead to $2 - \alpha = 3\bar{\nu}_n = (\nu_{\parallel n} + 2\nu_{\perp n})$ for all harmonics and thus the expectation that $\bar{\nu}_2 = \bar{\nu}_1 = \nu_{XY}$. If this were true, it would follow from $\gamma_n = (2 - \eta_n)\bar{\nu}_n$ that η_2 must be very different from $\eta_1 = \eta_{XY} \simeq 0.03$. Using $\bar{\nu}_2 = \nu_{XY} = 0.669$ and $\gamma_2 = 0.31 \pm 0.14$ predicted from harmonic scaling theory, one obtains $\eta_2 = 1.5 \pm 0.2$, while the experimental $\gamma_2 = 0.41 \pm 0.09$ yields $\eta_2 = 1.4 \pm 0.2$. In order to test this idea of large η_2 values, the $2q_0$ scattering peaks were reanalyzed with the form

$$S(2q_0) = \frac{k_B T \chi_2}{[1 + \xi_{\parallel 2}^2 (q_\parallel - 2q_0)^2 + \xi_{\perp 2}^2 q_\perp^2]^{1 - \eta_2/2}}. \quad (4)$$

As illustrated in Fig. 1, when η_2 was fixed at 1.4 not even a qualitative fit to the scattering profiles was possible. When η_2 was taken as a freely adjustable parameter at each temperature, η_2 values ranged from -0.3 to $+0.6$ with an average value of 0.25. Thus, as noted previously, the second-harmonic profiles are quite close to being pure Lorentzians. It should be noted that with $\eta_2 = 0.25$ scaling predicts $\bar{\nu}_2 = \gamma_2/(2 - \eta_2) = 0.23 \pm 0.06$ compared with the measured mean value $\bar{\nu}_2 = (\nu_{\parallel 2} + 2\nu_\perp)/3 = 0.26 \pm 0.04$. Thus γ_2, $\bar{\nu}_2$, and η_2 are internally consistent but anisotropic hyperscaling, $\nu_{\parallel 2} + 2\nu_{\perp 2} = 2 - \alpha$, is explicitly violated for the second-harmonic fluctuations. This analysis, of course, assumes that single power laws rather than some complicated crossover form represent the correct description of the critical divergences of the $2q_0$ fluctuations.

In summary, using synchrotron x-ray techniques it has been possible to measure the critical behavior above T_c associated with both the first- and second-harmonic critical fluctuations. We have also measured the relative intensities of the first- and second-harmonic density wave order parameter scattering below T_c. We find that the first-harmonic critical behavior is 3D XY-like, albeit with a small length anisotropy as is normally observed at N-Sm-A transitions. The second-harmonic susceptibility above T_c and the integrated Bragg intensity below T_c both are accurately predicted by the XY-model multicritical scaling theory [7,8]. However, the second-harmonic correlation lengths and exponents differ markedly from those characterizing the first harmonic. The scaling relation $\bar{\nu}_2(2 - \eta_2) = \gamma_2$ is obeyed but anisotropic hyperscaling, $\nu_{\parallel 2} + 2\nu_{\perp 2} = 2 - \alpha$, is severely violated. This result would appear to have important consequences for theories for all density wave systems. Is there a basic error in our current theoretical picture of density wave systems? Alternatively, is there a unique feature of the N-Sm-A_2 system which causes the violation of hyperscaling for the second-harmonic fluctuations [11]? Clearly, measurements of the higher-harmonic critical fluctuations in other density wave systems including most especially solid state materials such as $K_{0.3}MoO_3$, $NbSe_3$, and Cr are very important. Further guidance from theory would also be helpful.

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